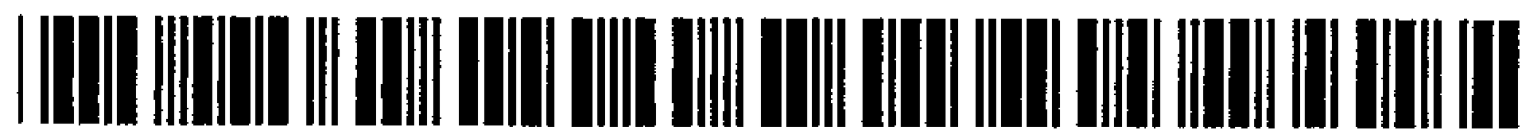

United States Patent [19]

Goela et al.

[11] **Patent Number: 5,604,151**

[45] **Date of Patent: Feb. 18, 1997**

[54] **CHEMICAL VAPOR DEPOSITION-PRODUCED SILICON CARBIDE HAVING IMPROVED PROPERTIES**

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[73] Assignee: **CVD, Incorporated**, Woburn, Mass.

[21] Appl. No.: **439,034**

[22] Filed: **May 11, 1995**

Related U.S. Application Data

[62] Division of Ser. No. 389,780, Feb. 16, 1995, which is a continuation of Ser. No. 159,915, Nov. 29, 1993, abandoned, which is a continuation of Ser. No. 979,965, Nov. 23, 1992, abandoned.

[51] **Int. Cl.**^{6} **H01L 21/20**

[52] **U.S. Cl.** **437/100**; 117/101; 117/104; 117/951

[58] **Field of Search** 117/104, 101, 117/951; 437/100

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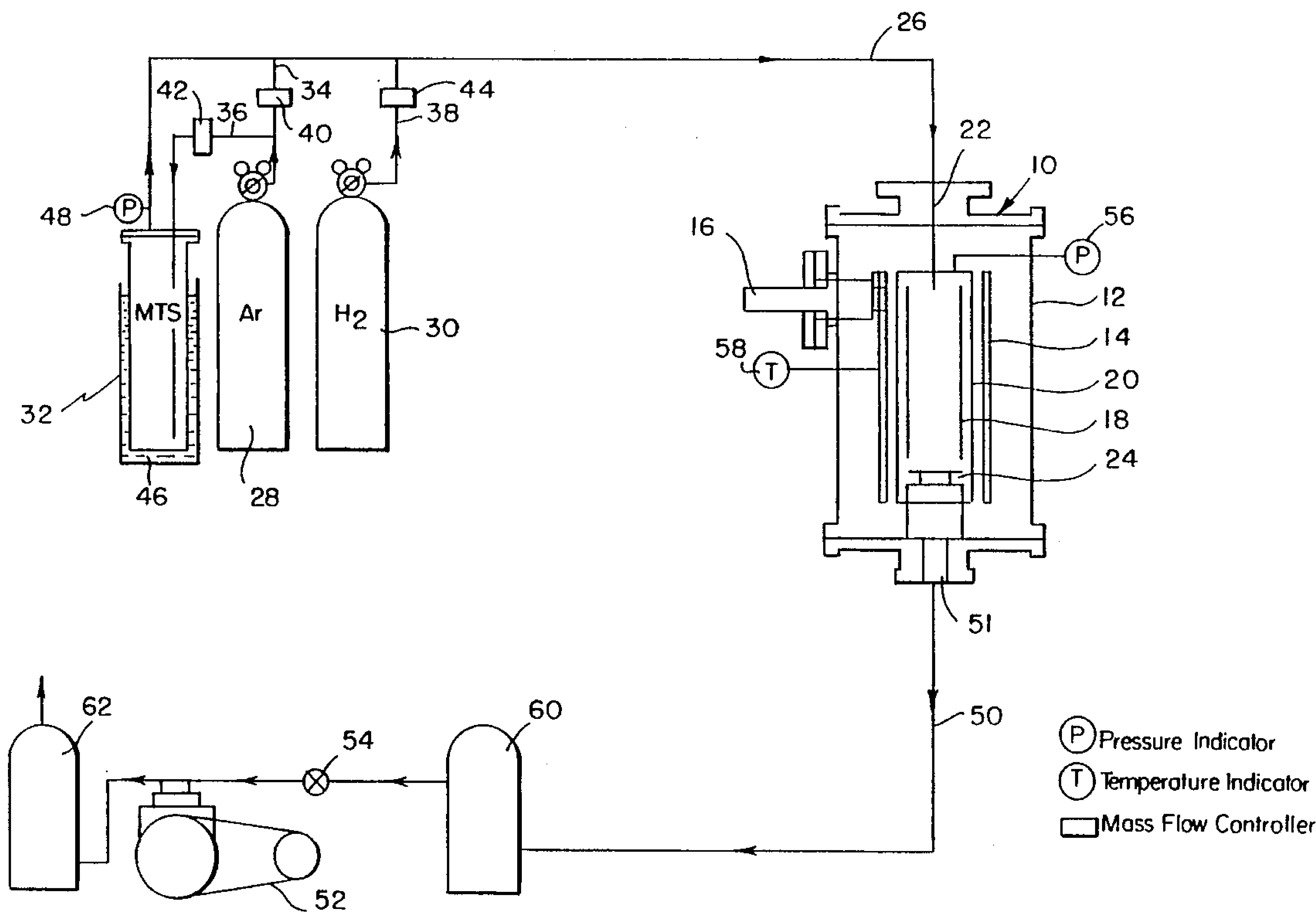
Primary Examiner—Robert Kunemund
Attorney, Agent, or Firm—Wayne E. Nacker; Gerald K. White

[57] **ABSTRACT**

β-silicon carbide which is optically transmitting in the visible and infrared regions is produced by chemical vapor deposition. Deposition conditions are temperatures within a 1400°–1500° C. range, pressure 50 torr or less, H_2/methyltrichlorosilane molar ratios of 4–30 and a deposition rate of 1 μm or less.

12 Claims, 4 Drawing Sheets



A schematic of CVD process used to fabricate SIC of Improved transmission.

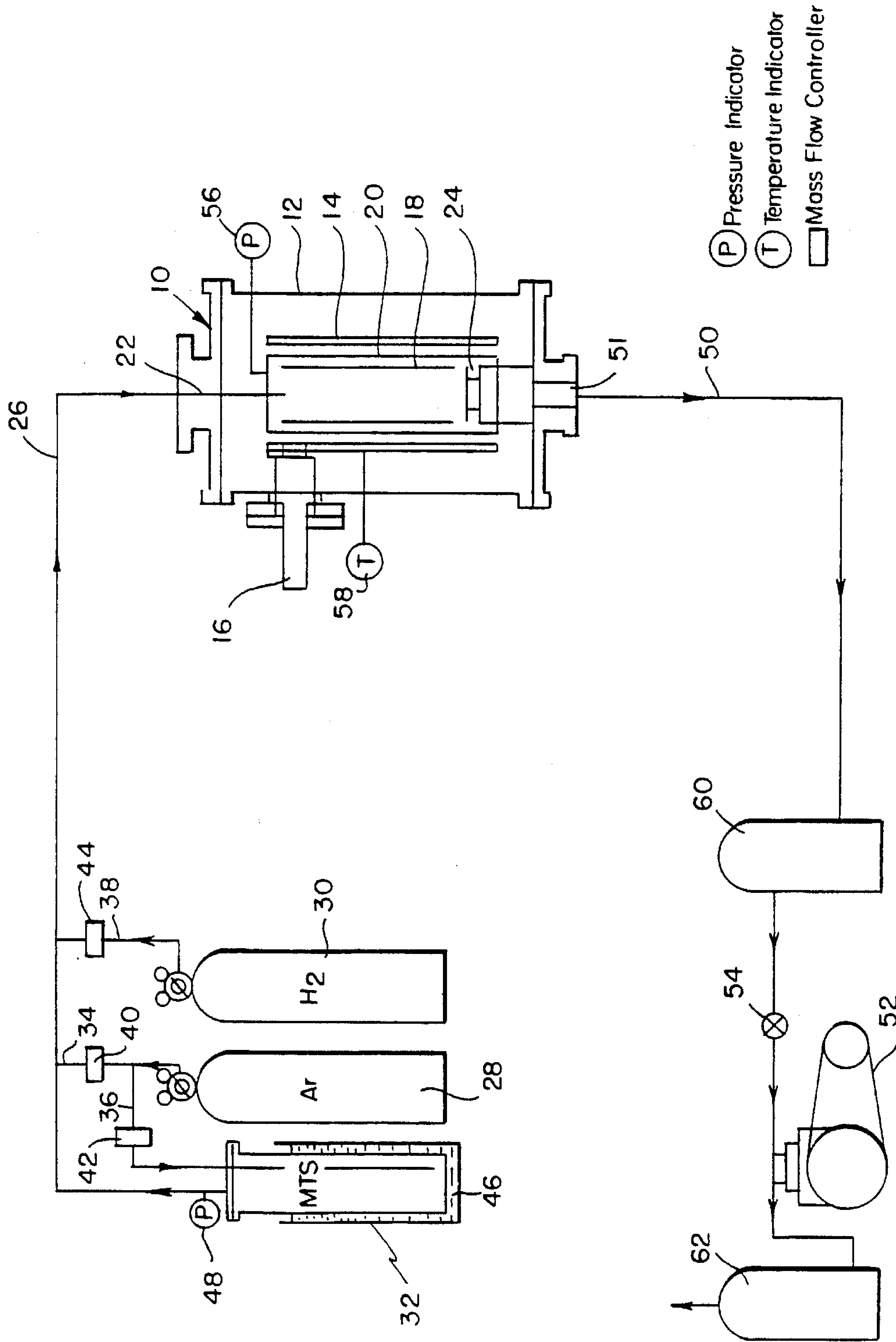
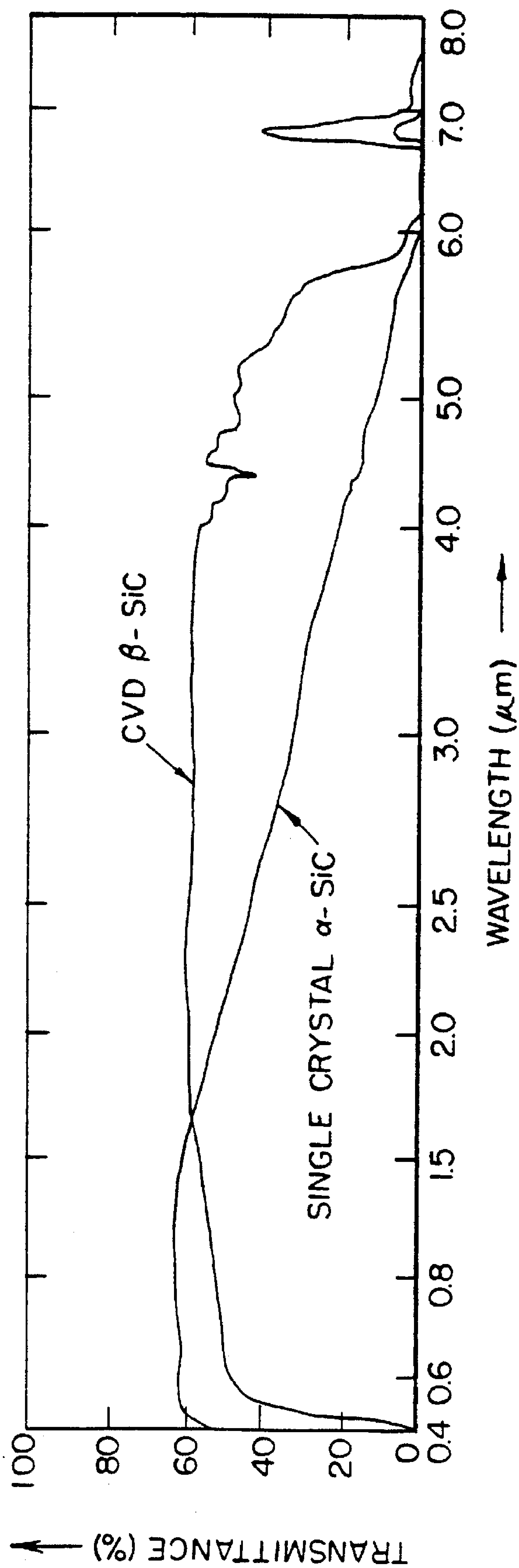


FIG. 1

A schematic of CVD process used to fabricate SIC of Improved transmission.



A comparison of transmission of CVD-βSiC (Run-9) with that of α -SiC single crystal.
Sample thickness = 0.012-inch.

FIG. 2

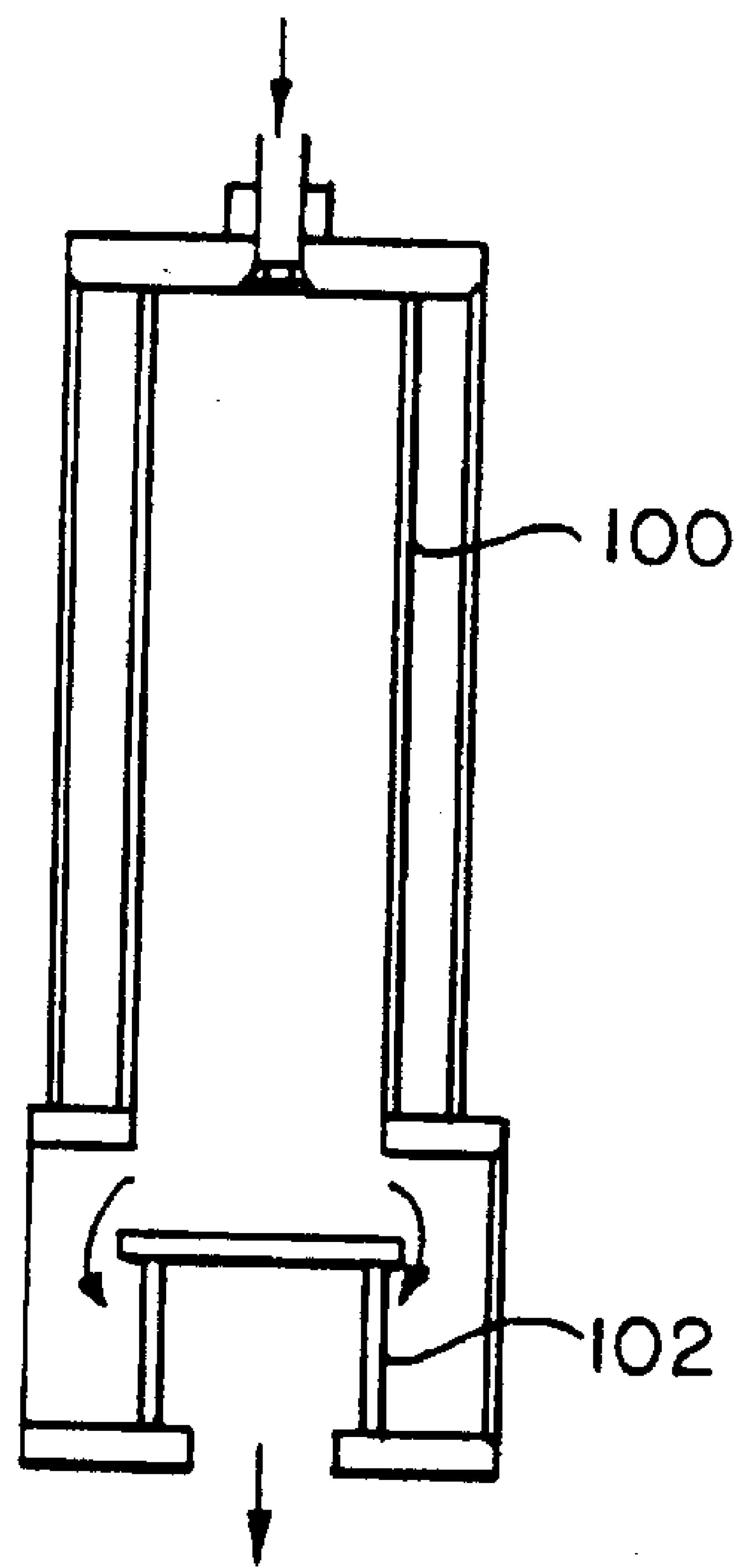


FIG.3(a)

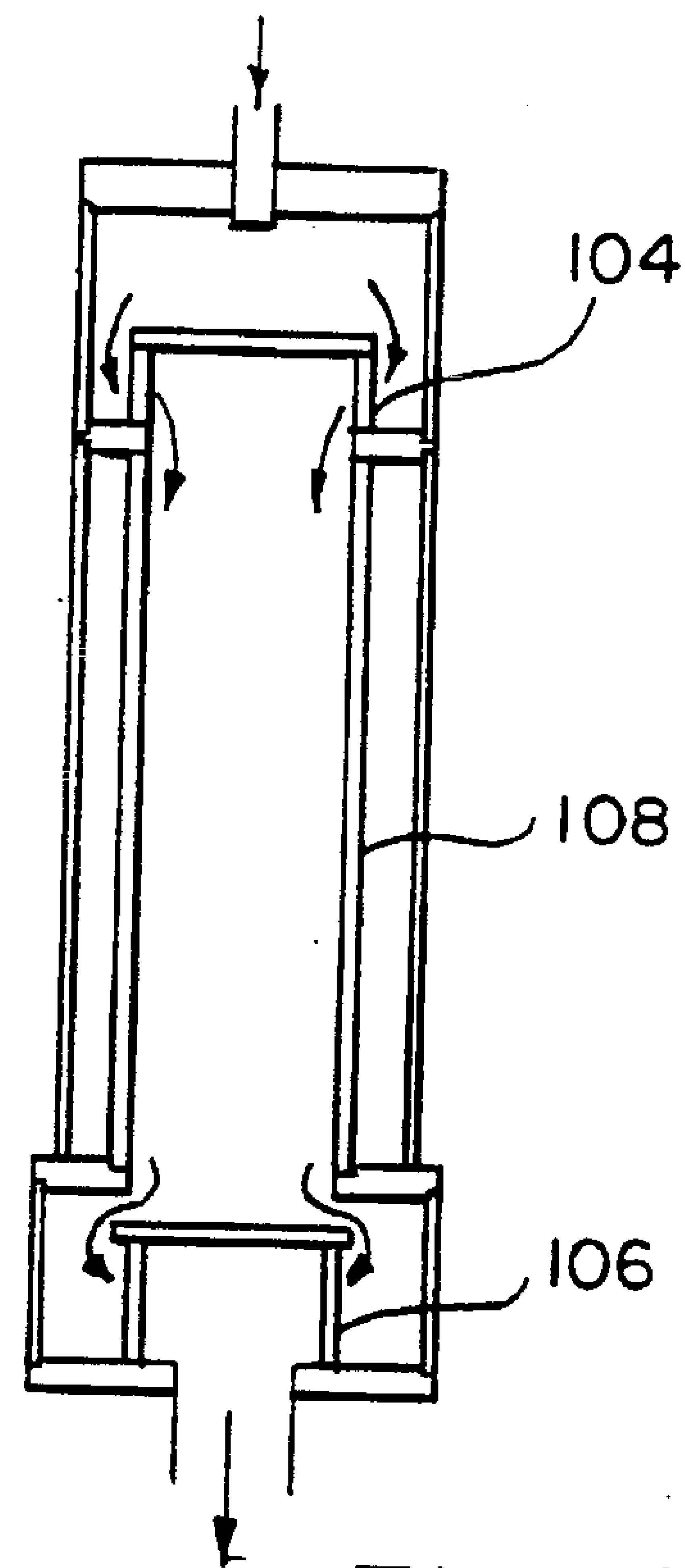


FIG. 3(b)

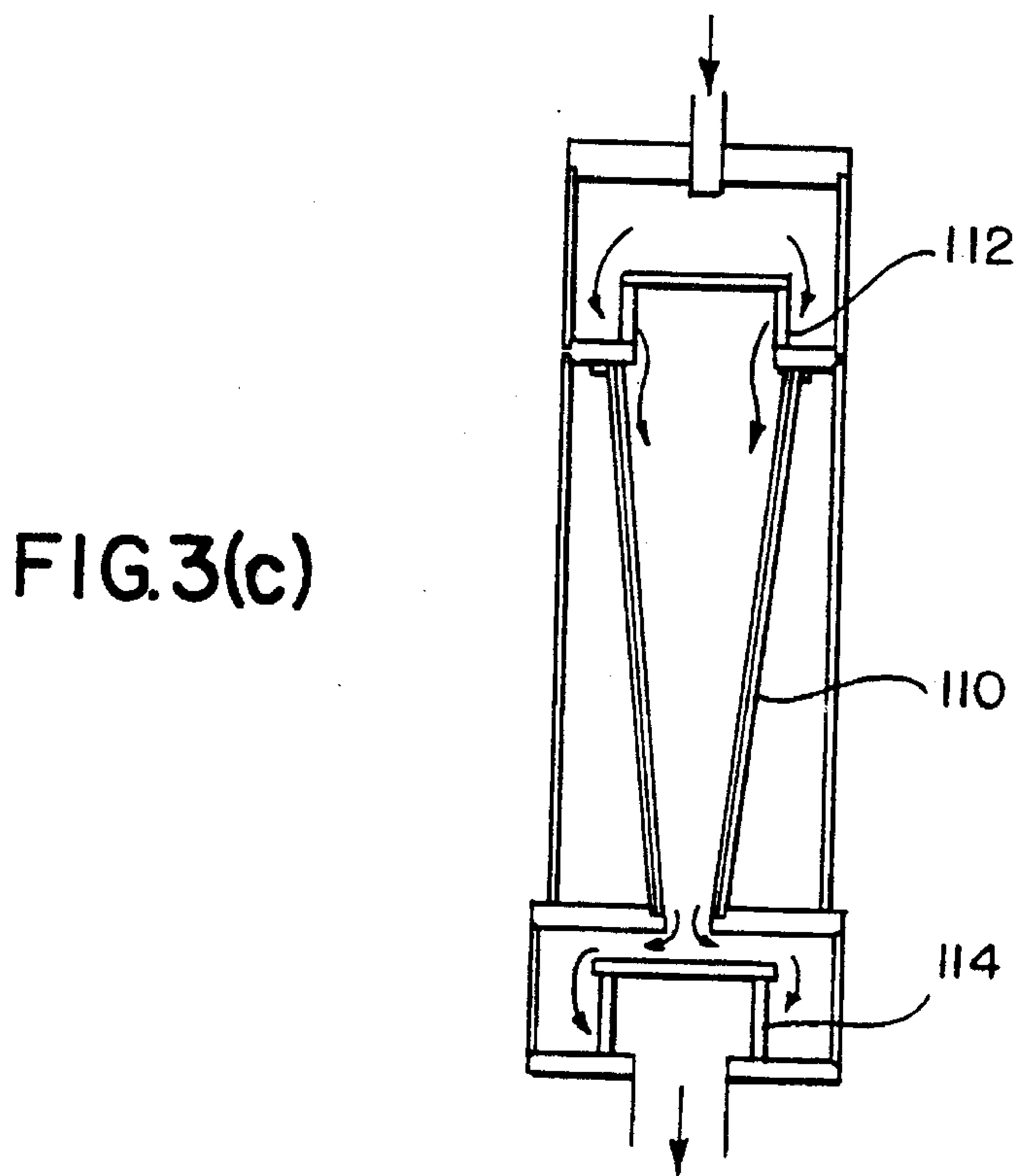
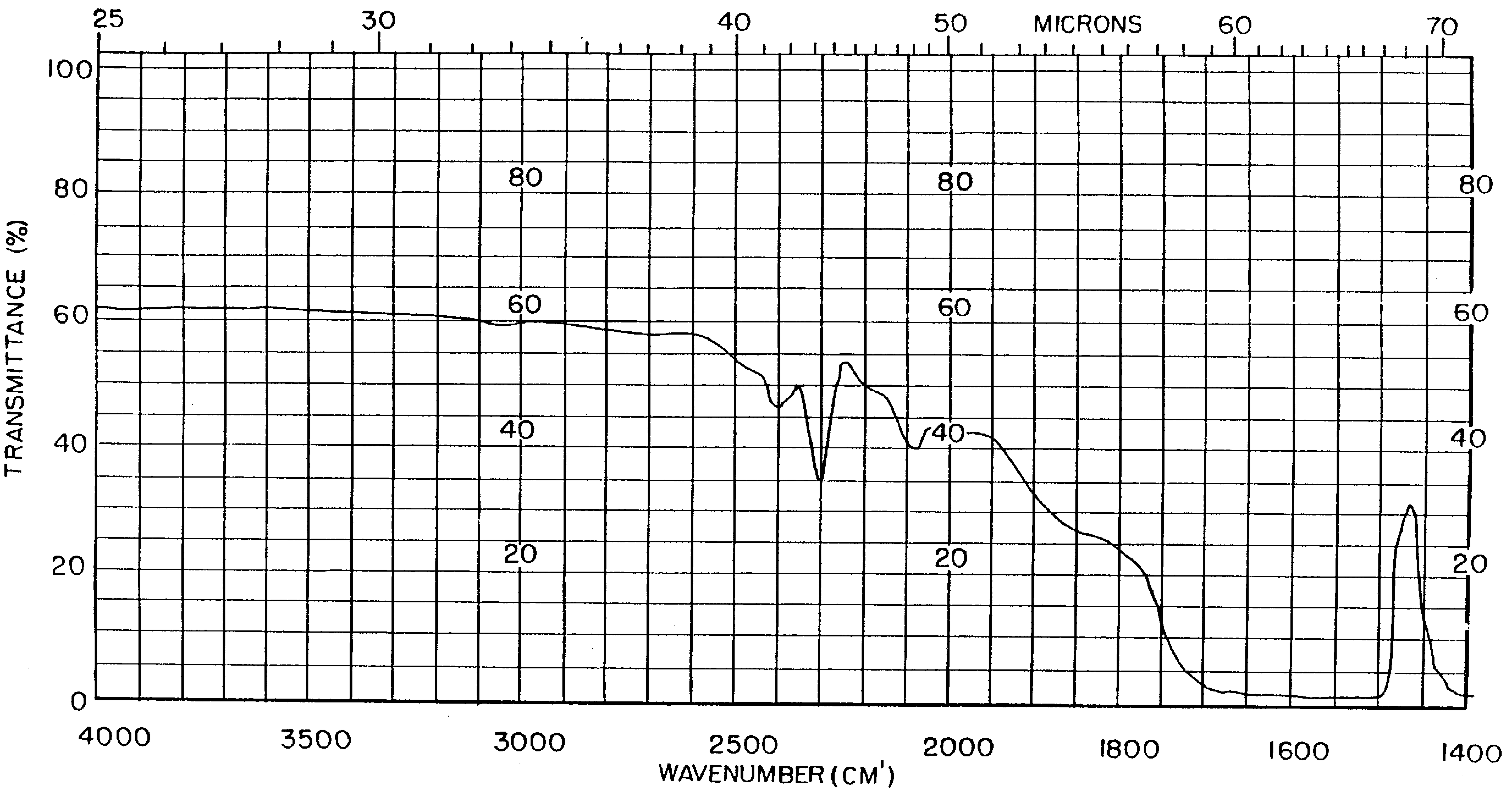


FIG.3(c)

Schematics of deposition set-ups used to fabricate Improved transmission β-SiC.



Transmission of CVD-βSiC in the wavelength range of 2.5-7.5 μm.
Material Thickness 0.022-inch, Run No. 10

FIG. 4

CHEMICAL VAPOR DEPOSITION-PRODUCED SILICON CARBIDE HAVING IMPROVED PROPERTIES

This is a divisional of U.S. application Ser. No. 08/389,780 filed on Feb. 16, 1995, which is a continuation of U.S. patent application Ser. No. 08/159,915 filed Nov. 29, 1993 (abandoned), which was a continuation of U.S. patent application Ser. No. 07/979,965 filed Nov. 23, 1992 (abandoned).

The present invention is directed to silicon carbide produced by chemical vapor deposition processes having improved optical properties, including improved optical transmission, purity, and electrical resistivity, and to a deposition process for producing such silicon carbide.

BACKGROUND OF THE INVENTION

While single crystal α-SiC exhibits some degree of optical transmission, polycrystalline β-SiC is substantially opaque. It would be desirable to provide β-SiC which optically transmits, particularly in the visible and infrared range. Optically transmitting SiC would have applications for lenses and domes, light detection and ranging (LIDAR) mirrors, solar collectors and concentrators, cathode covers (in the reactive ion etching systems), and astronomical mirrors. Single crystal α-SiC is unsuitable for such bulk applications due to its size limitation; thus, it would be desirable to produce optically transmitting β-SIC which can be produced in bulk.

Known bulk silicon carbide is almost invariably opaque, absorbing and scattering light in the visible and infrared regions of the spectrum. Methods of producing bulk SiC include sintering and hot pressing, slip casting and reaction bonding. These methods are unlikely candidates for producing optically transmitting SiC as they suffer from one or more of the following drawbacks: 1) they produce a multiphase material, e.g., include a Si phase, 2) the material is not theoretically dense, and/or 3) the material is not of high purity and may contain metallic impurities that degrade optical transmission.

A better candidate for producing optically transmitting SiC, either free-standing bulk SiC or thin films on a substrate surface, is SiC produced by chemical vapor deposition (CVD). However, most of the SiC previously produced by CVD is opaque, exhibiting considerable scattering and absorption in the visible and infrared. Applicants are aware of efforts by the U.S. Air Force and General Electric to improve the infrared transmission of SiC by improving process parameters, such as substrate temperature, flow rates, furnace pressure etc. These efforts met with limited success. Although SiC transmitted in the 2–5 μm (infrared spectrum range), the material exhibited considerable scattering which made it unsuitable for use in imaging applications.

It is a general object of the present invention to produce β-SiC in bulk or thin film form having improved optical transmission. Other objects include providing CVD-SiC having heretofore unachieved purity, and electrical resistivity.

SUMMARY OF THE INVENTION

Bulk, free-standing, silicon carbide, fabricated by chemical vapor deposition (CVD), is optically transmitting in the visible and infrared range. Specific deposition parameters are required to produce the optically transmitting silicon

carbide. This silicon carbide is highly pure, theoretically dense and has electrical resistivity in excess of SiC's previously known.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic of CVD apparatus used to fabricate optically transmitting β-SiC.

FIG. **2** is a graph comparing the transmission of CVD-β-SiC with the transmission of α-SiC.

FIGS. **3***a*, **3***b* and **3***c* illustrate different baffle/mandrel arrangements used within the deposition chamber of a furnace for the fabrication of CVD-β-SiC.

FIG. **4** is a transmission spectrum of a highly optically transmitting CVD-β-SiC.

DETAILED DESCRIPTION OF CERTAIN PREFERRED EMBODIMENTS

Herein, unless otherwise noted, optical properties of silicon carbide produced in accordance with the present invention are defined in terms of Attenuation Coefficients (cm^{-1}) at 0.6328 μm (visible-laser measured) and 3 μm (infrared-spectrophotometer measured). Attenuation coefficient is intended herein to include all optical losses, including both scattering and absorption. Attenuation coefficient is calculated as follows. If T, R, x are the transmittance, reflectance and material thickness, then the attenuation coefficient, β is calculated from the following equation

$$T = \frac{(1-R)^2 \exp(-\beta x)}{1 - R^2 \exp(-2\beta x)}$$

The reflectance is calculated from the refractive index (n).

$$R = \frac{(n-1)^2}{(n+1)^2}$$

The refractive index (n) is assumed to be 2.635 at 0.6328 μm and 2.555 at 3 μm.

Unless otherwise stated, properties of SiC produced in accordance with the invention are room temperature values, i.e., measured at 20°–28° C. (293°–301° K.). Although it is believed that thermal conductivity measurements are generally independent of the measuring technique, thermal conductivity values reported herein are those measured by flash-lamp techniques. Deposition chamber temperatures are measured by thermal probes within the deposition chamber placed closely adjacent the deposition site, e.g., a mandrel on which bulk free-standing SiC is to be deposited or a surface on which a film of SiC is to be deposited. Although the deposition site temperature may not be exactly that of the probe-measured location, experience has found that probes closely adjacent, but differently located relative to a deposition site are almost always within 10° C. of each other and generally within 5° C. of each other. Thus, the deposition site is presumed to be within 5°–10° C. of the probed deposition chamber temperature.

The SiC to which the invention pertains is bulk or free-standing, i.e., capable of being self-supported. This is to be distinguished from thin SiC films which are deposited upon a surface with the intent that the SiC remain permanently bonded thereto. To be free-standing, the SiC must generally be deposited to a thickness of upward of about 0.1 mm.

Silicon carbide produced in accordance with the present invention has an attenuation coefficient at 0.6328 μm of about 20 cm^{-1} or less, preferably about 10 or less, and more

preferably about 8 or less. The silicon carbide has an attenuation coefficient at 3 μm of about 20 cm^{-1} or less, preferably about 10 or less, more preferably about 8 or less and most preferably about 5 or less. It is believed that silicon carbide produced in accordance with the present invention is more optically transmitting at 0.6328 and 3 μm than any polycrystalline silicon carbide of the prior art. The silicon carbide in accordance with the invention is stoichiometric (1:1 Si:C ratio), 100% theoretical dense, and highly pure, i.e., about 5 ppm metallic impurities or less and preferably about 3.5 ppm metallic impurities or less. It is found that the higher is the purity, the greater is the optical transmittance of the SiC produced. Also high purity is very important for semiconductor furniture manufactured of CVD-SiC. High purity is achieved using high purity reaction materials, particularly O_2-free H_2 and contamination free grahite deposition set up. It has been demonstrated that distilling MTS from its as-purchased condition results in more optically transmitting CVD-deposited SiC.

Another feature of the SiC of the present invention is its very high bulk resistivity. Resistivity is an important attribute of material for electronic packaging. The upper limit of most non-doped SiC to date is about 100 ohm-cm, and CVD-SiC is not believed to have been consistently produced having resistivity of more than 100 ohm-cm. The resistivity of CVD-SiC according to the present invention has reached 4.53×10^4 ohm-cm. When SiC of such high electrical resistance is achievable, values lower than this value, yet still above that known in the prior art, is achievable, by introduction of impurities, e.g., through doping. Accordingly, novel CVD SiC is produced in accordance with the present invention having resistivity of 500 ohm-cm or greater, preferably 1000 ohm-cm or greater, and more preferably 10,000 ohm-cm or greater. Furthermore, the SiC produced in accordance with the invention is of the n-type, whereas most CVD-SiC is of the p-type. n-type is preferred as its resistivity tends to be constant over a broader temperature range.

Illustrated in FIG. **1** is an apparatus useful for fabricating CVD-β-SiC. Deposition is carried out within a furnace **10**. A stainless steel wall provides a cylindrical deposition chamber **12**. Heating is provided by a graphite heating element **14** which is connected to an external power supply by an electrode **16**. Graphite deposition mandrels are arranged within a graphite isolation tube **20** and gas is introduced by means of an injector **22** through the upper end of the isolation tube so that the reaction gases sweep along the mandrels **18**. One or more baffle(s) **24** is used to control the aerodynamics of gas flow through the furnace.

The line **26** which supplies the injector is fed by an argon cylinder **28**, a hydrogen cylinder **30**, and a MTS bubbler **32**. The argon is fed by lines **34** and **36** both directly to inlet line **26** and through the bubbler **32**. The hydrogen cylinder is connected by a line **38** to the inlet line **26**. Argon flow through lines **32** and **36** and hydrogen flow through line **38** are controlled by mass flow controllers **40**, **42** and **44**. The MTS cylinder **32** is maintained at a constant temperature by a constant temperature bath **46**. A pressure gauge **48** is connected to a feed back loop which controls the gas pressure of the bubbler **32**.

An outlet line **50** is connected to a bottom outlet port **51**. Pressure within the deposition chamber **12** is controlled by a vacuum pump **52** which pulls gases through the chamber and a furnace pressure control valve **54** operably connected to the vacuum pump. The temperature and pressure within the deposition chamber **12** are measured by a thermal probe **58** and a pressure indicator **56**. Exhaust gases are passed through a filter **60** to remover particulate material upstream of the pressure control valve and through a scrubber **62** downstream of the vacuum pump to remove HCl.

As discussed below in the examples, particularly with respect to FIGS. *3a*, *3b* and *3c*, the arrangement of baffles may be varied to produce desired results. The results discussed below with respect to FIGS. *3a*, *3b* and *3c* are particular to the furnace in which the SiC was deposited and may vary from furnace to furnace and also the configuration of the mandrel or substrate on which SiC of desired configuration is to be deposited.

To obtain optically transmitting CVD-deposited β-SIC, a deposition chamber temperature of between about 1400 and about 1500° C., preferably between about 1400 and about 1450° C. is employed. The deposition chamber pressure is about 50 torr or lower, preferably about 10 torr or lower and most preferably about 5 torr or lower. The H_2/MTS ratio is from about 4 to about 30, preferably from about 10 to about 20. The deposition rate is about 1 micron per minute or less; it is believed that this very low deposition rate is critical to obtain β-SIC with good optical transmittance. The rate at which the deposition surface is swept by the reactant gases also appears to affect the optical transmittance of the deposited SiC. Although optically transmitting SiC has been produced with average flow velocities of about 10 cm/sec, it is preferred that flow velocities be at least about 300 cm/sec, and more preferably at least about 1000 cm/sec. Sweep velocity, which is the gas velocity at the deposition surface, is a function not only of the flow rate of gases into the furnace, but of the furnace design and orientation of the deposition surface(s) within the deposition chamber of the furnace.

HCl is a reaction product of the deposition of SiC using MTS and H_2/MTS as the reaction gases. It is found that adding gaseous HCl to the gas stream that is introduced into the reaction chamber further improves the optical transmission of the CVD-β-SiC which is produced. To have a significant effect on transmission of the SiC, the HCl/MTS molar ratio is generally at least about 0.2.

The invention will now be described in greater detail by way of specific examples in the experiments described below.

EXAMPLE 1

Several depositions of SiC were performed in a CVD reactor to fabricate CVD-SiC with improved transmission. In these depositions, the CVD process conditions and the deposition set-up were varied to optimize the vis-IR transmission of CVD-SiC. The process conditions used were: substrate temperature: 1400°–1470° C., furnace pressure: 3–200 torr, flow rates—MTS: 0.1–2.8 slpm (standard liters per minute), H_2: 0.5–5.8 slpm. H_2/MTS molar ratio: 4–30, and average flow velocity =14–1260 cm/sec.

The CVD-SiC was characterized for vis-IR transmission. The SiC transmission was determined to be dependent upon MTS purity, CVD process conditions and CVD deposition geometry. The commercially available MTS of 99% purity contains metallic impurities which end up in the CVD-SiC and degrade its near-IR transmission. Distillation of MTS in a narrow temperature range around its boiling point has resulted in fabricating SiC which exhibits good transmission in the infrared region.

Table 1 below shows the attenuation coefficient values for CVD-SiC at 0.6328 μm and 3 μm as a function of furnace pressure. It is seen that as the pressure decreases from 200 torr to 10 torr, both visible and infrared attenuation coeffi-

cients decrease, i.e., transmittance in both visible and infrared regions increase. Although Run #11 (furnace pressure=3 torr), material showed an increase in attenuation coefficient in comparison to Run #7 (furnace pressure=10 torr), this increase may be due to the deposition set-up which was changed.

The effects of varying other CVD process parameters on transmission were less clear. Optimum results were obtained for the following process conditions. Substrate temperature: 1425° C., Furnace pressure: 10 torr, Flow rate: MTS=0.19 slpm, H_2=2.8 slpm, Ar=1.0 slpm, H_2/MTS molar ratio=15 and average flow velocity=365 cm/sec.

Three deposition set-ups were tried in an effort to maximize the transmission of CVD-SiC. These set-ups are shown in FIG. **3***a*, **3***b* and **3***c*. All these set-ups yielded CVD-β-SiC with improved transmission at different parts of the deposition region. Two set-ups (FIGS. **3***a,b*) used four rectangular mandrel plates, 3.5 in.-wide×12 in.-long, arranged in the form of an open square box.

The deposition set-up of FIG. **3***a* consisted of a mandrel box **100** at the end of which was placed a graphite baffle **102**. In this case, porous material was deposited on the mandrel while dense and good quality β-SiC was obtained on the baffle. It is believed that the porous material was deposited because (i) the reagents were "cold," i.e., there was considerable temperature difference between the mandrel and the gaseous reagents and (ii) the reagent sweep speed on the mandrel walls was small. This explanation is consistent with the observation that the material on the upper half of the mandrel was more porous than on the lower half.

In FIG. **3***b* two baffles were used, one **104** before and the other **106** after the mandrel box. The function of the first baffle **104** is to preheat the reagents and direct the gas close to the mandrel walls to increase reagents sweep speed along the mandrel box **108**. This deposition set-up produced CVD β-SiC with good vis-IR transmission. The "best" material was produced on the upper half of the the mandrel box. The deposited material on other areas had better transmission than that produced at other CVD conditions.

In the deposition set-up of FIG. **3***c*, the two walls of the mandrel box **110** were tapered. The cross-section of the mandrel box was a square 3.5 in.×3.5 in. on the top end and a rectangle 3.5 in.×1.05 in. at the bottom end. The aim of using this tapered box was to continuously reduce the cross-section and thus increase the flow velocity to study its effect on the quality of the material. This set-up also employed a baffle **112** before and a baffle **114** after the mandrel box. Although this configuration also produced good optical quality CVD-SiC, considerable stress in the material was observed and the deposited material exhibited substantial bowing.

TABLE 1

Attenuation Coefficient of CVD-βSIC as Function of Furnace Pressure

Run No.	Furnace Set-Up	Furnace Pressure (Torr)	Attenuation Coefficient (cm^{-1}) @ 0.6328 μm	@ 3 μm	Avg Velocity cm/sec
2	3a	200	30	40	49
3	3b	200	66	24	21
4	3b	40	19	21	197
5	3c	20	16	14	272–761
7	3b	10	7.3	3.5	365
11	3b	3	—	7.6	1260

EXAMPLE 2

Addition of HCl to the reaction mixture is found to suppress formation of Si-rich SiC. The CVD process conditions were: substrate temperature=1413°–1423° C., Furnace pressure: 3–7 torr, flow rates—H_2: 2.8 slpm, MTS: 0.19 slpm, Ar: 1.0 slpm, HCl: 0.15–6.0 slpm, H_2/MTS molar ratio: 15, HCl/H_2 molar ratio=0.054–0.21 and an average flow velocity: 540–1260 cms^{-1}. The deposition set-up used was the two-baffle configuration of FIG. **3***b*. Table 2 below lists the attenuation coefficient values that were obtained when HCl was added to the reagent mixture. A comparison of attenuation coefficient for Run #10 and #11 (Table 1) clearly shows improved optical transmission values when HCl is added. Further, similar to Example 1, the vis-IR transmittance of CVD-SiC increased as the furnace pressure decreased.

TABLE 2

Attenuation Coefficient of CVD-βSIC when HCl is Added to the Reaction Mixture

Run No.	Furnace Set-Up	Furnace Pressure (Torr)	Attenuation Coefficient (cm^{-1}) @ 0.6328 μm	@ 3 μm	Avg Velocity cm/sec
9	3b	7	7.4	2.8	540
10	3b	3	6.9	2.1	1260

FIG. **2** shows a comparison of transmission of β-SiC with that of commercially available α-SiC single crystal sample. Both samples are 0.012-inch thick. It is seen that CVD-β SiC performs considerably better than single crystal α-SiC in the near-IR region while the latter material performs better in the visible region.

FIG. **4** shows infrared transmission of CVD-SiC when HCl is added to the reaction mixture (Run #10). The thickness of the sample was about 0.022-inch. 60% transmission is seen in the near IR region which corresponds to an attenuation coefficient of 2.1 cm^{-1} at 3 μm. This is believed to be the lowest value of specular attenuation coefficient that has ever been achieved for polycrystalline CVD-βSiC free-standing sample. This material was also characterized for hardness and fracture toughness and yielded values of Vickers hardness (Kg mm^{-2})=2700±58.8 with 1 Kg load and fracture toughness (MN $m^{-3/2}$)=2.23±0.043. These values are typical of CVD-SiC. Thus, an improvement in optical properties has been obtained without degrading other properties such as hardness and fracture toughness.

While the invention has been described in terms of certain preferred embodiments, modifications obvious to one with ordinary skill in the art may be made without departing from the scope of the invention.

Various features of the invention are set forth in the following claims.

What is claimed is:

1. In a method of producing optically transmitting, free-standing, polycrystalline, β-SiC wherein a chemical vapor deposition having a deposition chamber and a mandrel surface therein for deposition of SiC are provided, introducing methyltrichlorosilane and H_2 gas into said deposition chamber under conditions which pyrolytically deposit silicon carbide on said surface, the improvement wherein said conditions comprise a deposition chamber temperature of between about 1400° C. and about 1500° C. a deposition chamber pressure of about 50 torr or less, a H_2/methyltrichlorosilane molar ratio of between about 4 and about 30, a deposition rate of about 1 micron per minute or less, and HCl also being introduced into said deposition chamber in a HCl/methyltrichlorosilane ratio of at least about 0.15.

2. A method according to claim **1** wherein said pressure is about 10 torr or less.

3. A method according to claim **1** wherein said pressure is about 5 torr or less.

4. A method according to claim **1** wherein said temperature is between about 1400° C. and about 1450° C.

5. A method according to claim **1** wherein said H_2/methyltrichlorsilane ratio is between about 10 and about 20.

6. A method of producing optically transmitting, free-standing polycrystalline, β-SiC comprising,

providing a furnace having a tubular isolation chamber with a cylindrical sidewall, gas injector means disposed axially at on end of said isolation chamber and gas outlet means at the opposite end of said isolation chamber, and means disposed downstream of said inlet means for interdicting the flow of gas from said injector means to said outlet means and directing the flow of gas laterally to said sidewall,

disposing within said isolation chamber a deposition surface, said deposition surface being disposed parallel to the axis of said isolation chamber and downstream of said interdicting means,

introducing through said injector means and into said isolation chamber methyltrichlorosilane and H_2 gas under conditions which pyrolytically deposit silicon carbide on said deposition surface, said conditions comprising a deposition temperature of between about 1400° C. and about 1500° C., a deposition pressure of about 50 torr or less, a H_2/methyltrichlorosilane molar ratio of between about 4 and about 30, and a deposition rate of about 1 micron per minute or less.

7. A method according to claim **6** wherein said pressure is about 10 torr or less.

8. A method according to claim **6** wherein said pressure is about 5 torr or less.

9. A method according to claim **7** wherein said temperature is between about 1400° C. and about 1450° C.

10. A method according to claim **7** wherein said H_2/methyltrichlorsilane ratio is between about 10 and about 20.

11. A method according to claim **8** wherein HCl is also introduced into said isolation chamber at a HCl/methyltrichlorosilane molar ratio of at least about 0.15.

12. A method according to claim **7** further including disposing means downstream of said deposition surface and upstream of said outlet means for interdicting the flow of gas from said injector means to said outlet means and directing the flow of gas laterally to said sidewall.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,604,151

DATED : February 18, 1997

INVENTOR(S) : Goela et al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Col. 3, line 12, delete "is" (both occurrences)

Col. 4, line 34, delete "/MTS" after "H_2"

Col. 7, line 8, insert a comma before "polycrystalline"

Col. 8, line 11, "claim 7" should be "claim 6"
line 13, "claim 7" should be "claim 6"
line 15, "claim 7" should be "claim 6"
line 18, "claim 7" should be "claim 6"

Signed and Sealed this

Twenty-first Day of October 1997

Attest:

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks